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Liquid-liquid extraction of Th(IV) with Cyanex302

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Th(IV) was quantitatively extracted from $1\cdot10^{-3}$M HNO_3 using $1\cdot10^{-3}$M Cyanex302 in xylene and was stripped from the organic phase with 5M HCl. The effect of different parameters affecting the extraction was systematically studied to achieve optimum conditions for the extraction of thorium. Based on the data some separations of thorium from binary and complex mixtures and its recovery from monazite sand were achieved. The method is reproducible with a relative standard deviation of 0.4%.

Introduction

Thorium is used in a wide array of products and processes, for example in the production of ceramics, carbon arc lamps, alloys, in mantles and also as a source of nuclear energy. Thus the separation, isolation and recovery of thorium have its own importance. Liquid-liquid extraction has been the most commonly used technique for the separation and recovery of thorium. The organophosphorus compounds are an important class of extractants studied for thorium. Neutral oxygen donating reagents such as tributyl phosphate (TBP),[1,2] trioctyl phosphine oxide (TOPO),[3,4] Cyanex923 (a mixture of four trialkyl phosphine oxides),[5] tris-(2-ethyl hexyl) phosphate (TEHP)[6] and triphenyl phosphine oxide (TPPO)[7] were reported for extraction of thorium. Amongst the acidic organophosphorous compounds, the extraction of thorium was previously studied with bis(2-ethyl hexyl) phosphoric acid (HDEHP) and bis(2-ethyl hexyl) phosphinic acid (PIA8),[8] dibutyl dithio phosphoric acid,[9] dialkyl dithio phosphoric acid,[10] and 2-ethyl hexyl phosphonic acid mono 2-ethyl hexyl ester (PC-88A).[11] The interaction of organophosphorous compounds with TBP for thorium extraction was also studied.[12] These methods had certain limitations such as, the use of salting out agents,[2,4] multistage stripping,[5] use of organic acid media,[6,7] interferences from various ions[7] and high reagent and stripping acidity.[8]

Cyanex302 [bis(2,4,4-trimethyl pentyl)monothio phosphinic acid] due to its poor aqueous solubility, complete miscibility with common organic diluents and resistance to hydrolysis[13] offers considerable advantages over other extractants for commercial implementation of the extraction process. Cyanex302 has been established as a selective extractant for extractive separation of various elements[14] but the systematic studies using Cyanex302 for the quantitative extraction of thorium are lacking. The factors influencing extraction using a liquid cation-exchanger are the acidity of the extractant and aqueous phase acidity, the concentration of the extractant and nature of diluent. Hence, by controlling one or more parameters influencing extraction, selective extraction of the desired element can be achieved. The present work using Cyanex302 was undertaken to optimize the conditions for the quantitative extraction of thorium for its analytical application.

Experimental

Instrumentation

A wrist action flask shaker (General Trading Corporation India) was used for equilibration. A Digispec 110-D visible spectrophotometer (Feedback India Ltd.), an atomic absorption spectrophotometer, AAnalyst 200 (Perkin Elmer) and an inductively coupled plasma emission spectrophotometer (ICP-AES GBC 8440 Plasma Lab) were employed for determining metal ion concentration. An Elico LI-120 digital pH meter (Elico India, Ltd.) was used for pH adjustment.

Reagent and chemicals

A stock solution of Th(IV) was prepared by dissolving 1.58 g of $Th(SO_4)_2\cdot9H_2O$ in 250 ml of distilled water containing HNO_3 to prevent hydrolysis. The solution was standardized volumetrically[15] and a working solution containing Th(IV) (20 $\mu g\cdot ml^{-1}$) was prepared by appropriate dilution. Arsenazo III (S.D. Fine Chemicals) was prepared as a 0.1% (w/v) solution. Cyanex302, obtained as a gift sample from Cytec Canada was used without further purification. All reagents and chemicals used were of A.R. grade.

Extraction procedure

An aqueous phase containing 20 μg of Th(IV) in $1\cdot10^{-3}$M HNO_3 was equilibrated with 10 ml of $1\cdot10^{-3}$M Cyanex302 in xylene for 10 minutes in a separating funnel using a wrist action flask shaker. The phase volume ratio was maintained at 1 : 1. The two phases

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were allowed to settle and the organic phase containing Th(IV) was stripped with 5M HCl and determined in the aqueous phase with Arsenazo III at 660 nm.[16] The amount of Th(IV) was calculated from the calibration curve. The distribution ratio (D) was calculated from the percentage of thorium extracted in the organic phase. The reproducibility of the method evaluated for Th(IV) determination in six replicate experiments had a R.S.D. of 0.4%.

Results and discussion

Optimization of extraction conditions

Effect of nitric acid concentration: The extraction of Th(IV) was studied from $1\cdot10^{-4}$M–2M HNO_3 (Table 1) with $1\cdot10^{-3}$M Cyanex302 in xylene. The extraction of thorium increased with the increase in the concentration of nitric acid and decreased beyond $1\cdot10^{-3}$M HNO_3. The extraction of Th(IV) was 99.1% with $1\cdot10^{-3}$M HNO_3 possibly due to the formation of cationic species of thorium at this concentration of nitric acid extractable with Cyanex302. Hence, further studies were carried out using $1\cdot10^{-3}$M HNO_3 as the aqueous phase.

Effect of diluents: Various organic solvents were studied as diluents for Cyanex302 (Table 2). Quantitative extraction of Th(IV) was possible using xylene as a diluent for Cyanex302. Hence, $1\cdot10^{-3}$M Cyanex302 in xylene was used in all the studies.

Effect of Cyanex302 concentration: Th(IV) was extracted with different concentrations ($1\cdot10^{-4}$M–$2\cdot10^{-3}$M) of Cyanex302 in xylene (Table 3). Quantitative extraction was achieved from $1\cdot10^{-3}$M Cyanex302. Therefore, the optimum concentration of extractant selected was $1\cdot10^{-3}$M Cyanex302 in xylene.

Time of extraction: The extraction of Th(IV) was examined for various times of equilibration. The extraction with 5, 10, 15 and 20 minutes of shaking was 96.0%, 99.1 %, 97.9 % and 93.3% respectively, hence, a 10-minute time of equilibrium was used in all the experiments.

Influence of stripping agents: Various mineral acids such as hydrochloric acid, nitric acid and sulphuric acid were used as stripping agents for Th(IV). It was observed that Th(IV) was quantitatively stripped with 5M HCl, hence, 5M HCl was used as a stripping agent in all the studies (Fig. 1).

Nature of the extracted species

To evaluate the nature of extracted species, Th(IV) was extracted with different concentrations of Cyanex302 in xylene under the optimum extraction conditions and the distribution ratio was evaluated. The plot of log D vs. log [Cyanex302] had a slope of 1.8 (Fig. 2) hence, the molar ratio of thorium to the extractant is 1:2. Similar results have been reported earlier.[12]

Effect of diverse ions

The influence of alkali, alkaline earths, transition metals and rare earths on the extraction of Th(IV) under its optimum extraction conditions was studied. The tolerance limit was set as the amount of foreign ion causing not more than ±2% change in the recovery of Th(IV). The results presented in Table 4 indicate that Th(IV) can be quantitatively extracted in the presence of large number of foreign ions including rare earth elements. Thus the method developed is specific for Th(IV).

Separation of Th(IV) from binary mixtures

Various binary mixtures containing Th(IV) with commonly associated elements were devised by selectively extracting Th(IV) into the organic phase under its optimum extraction conditions (Table 5). The elements remaining unextracted in the aqueous phase were determined by AAS or by ICP-AES. The separation factor (β) was calculated as the ratio of the distribution ratio:

$$(D = [\mathrm{M}]_{\mathrm{Org.}} : [\mathrm{M}]_{\mathrm{Aq.}})$$

of Th(IV) to the metal ($\beta = D_{\mathrm{Th}} : D_{\mathrm{M}}$). The results indicate that in all these separations relatively high separation factors with a good reproducibility was achieved.

Table 1. Extraction of Th(IV) as a function of nitric acid concentration

HNO_3, M	Extraction, %	Distribution ratio (D)
$1\cdot10^{-4}$	96.8	30.2
$1\cdot10^{-3}$	99.1	110.1
$1\cdot10^{-2}$	87.3	6.9
$1\cdot10^{-1}$	67.2	2.0
1.0	38.0	0.6
2.0	32.7	0.5

Th(IV) = 20 μg.
Organic phase = $1\cdot10^{-3}$M Cyanex302 in xylene.
Stripping agent = 5M HCl.

Table 2. Effect of diluents

Diluent	Extraction, %	Distribution ratio (D)
Xylene	99.1	110.1
Toluene	93.2	13.7
Benzene	91.1	10.2
Cyclohexane	84.4	5.4
Chloroform	83.2	5.0
Carbon tetrachloride	73.8	2.8

Aqueous phase = 20 μg Th(IV) in $1\cdot10^{-3}$M HNO_3.
Organic phase =$1\cdot10^{-3}$M Cyanex302.
Stripping agent = 5M HCl.

Table 3. Effect of Cyanex302 concentrations

Cyanex302, $\times 10^{-3}$M	Extraction, %	Distribution ratio (*D*)
0.1	25.2	0.3
0.2	40.0	0.7
0.3	46.0	0.9
0.4	52.4	1.1
0.5	76.9	3.3
0.6	81.3	4.3
0.7	86.0	6.1
0.8	88.0	7.3
0.9	94.5	17.2
1.0	99.1	110.1
2.0	99.1	110.1

Aqueous phase = 20 μg Th(IV) in $1 \cdot 10^{-3}$M HNO_3.
Stripping agent = 5M HCl.

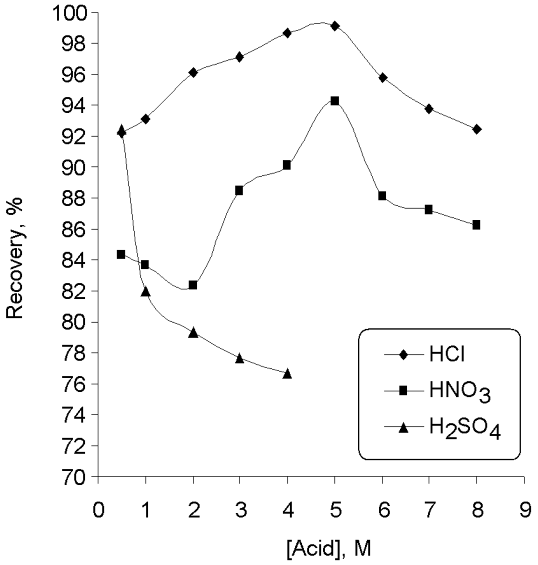

Fig. 1. Effect of stripping agents on the recovery of Th(IV); aqueous phase = 20 μg Th(IV) in $1 \cdot 10^{-3}$M HNO_3, organic phase = $1 \cdot 10^{-3}$M Cyanex302 in xylene

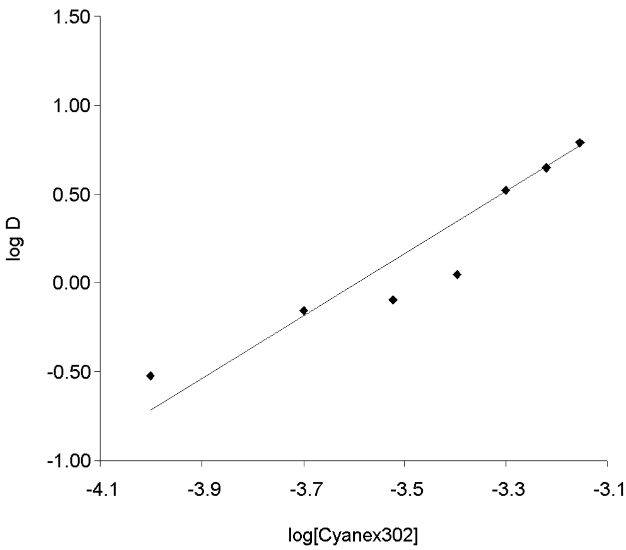

Fig. 2. Nature of the extracted species; aqueous phase = 20 μg Th(IV) in $1 \cdot 10^{-3}$M HNO_3, stripping agent = 5M HCl

Table 4. Effect of diverse ions

Cation	Tolerance limit,* μg
Na^+	100
K^+	4500
Ca^{2+}	5000
Mg^{2+}, Cu^{2+}	50
Mn^{2+}, Co^{2+}	500
Ni^{2+}, Cd^{2+}, Cr^{6+}	20
Ce^{4+}	60
Nd^{3+}	40
Dy^{3+}, Yb^{3+}, Pr^{3+}	20
La^{3+},Y^{3+}	30

Aqueous phase = 20 μg Th(IV) in $1 \cdot 10^{-3}$M HNO_3.
Organic phase = $1 \cdot 10^{-3}$M Cyanex302.
Stripping agent = 5M HCl.
* Average of six replicate analysis.

Table 5. Binary separations

Metal ion	Amount added, μg	Metal ion unextracted,* %	Recovery of Th(IV),* %	Separation factor (*β*)
Na(I)	100	98.7 ± 0.1	99.3 ± 0.1	11515
K(I)	4500	98.8 ± 0.3	98.9 ± 0.3	7163
Ca(II)	5000	99.7 ± 0.3	99.4 ± 0.2	47433
Mn(II)	500	98.8 ± 0.3	98.7 ± 0.2	6301
Co(II)	500	99.7 ± 0.2	98.9 ± 0.3	32197
Ni(II)	20	98.7 ± 0.2	98.9 ± 0.3	6525
Cd(II)	20	98.7 ± 0.2	98.2 ± 0.1	5948
La(III)	30	98.8 ± 0.3	98.8 ± 0.2	6576
Nd(III)	40	98.6 ± 0.2	98.1 ± 0.1	3774
Dy(III)	20	98.8 ± 0.2	98.7 ± 0.2	6338
Pr(III)	20	99.2 ± 0.3	98.8 ± 0.2	10154
Y(III)	20	98.9 ± 0.3	98.8 ± 0.3	7084

* Average of six replicate analysis with % R.S.D.

Applications

Separation of Th(IV) from multi-component mixtures

The applicability of the method for isolation and determination of Th(IV) from complex mixtures was studied (Table 6). In the synthetic mixtures, Th(IV) was extracted under the optimum extraction conditions and the aqueous phase was analyzed for the other elements using AAS or ICP-AES. The recovery of other elements was more than 98% as they remained unextracted in the aqueous phase. Th(IV) was quantitatively recovered in all mixtures.

Recovery of Th(IV) from monazite sand

0.1 g of monazite sand sample was digested at 250 °C with concentrated sulphuric acid.[17] The resulting rare earths and Th(IV) were repeatedly extracted with 1:10 H_2SO_4 and made to a suitable volume. The results for the extraction and determination of Th(IV) from a known aliquot of this sample solution are presented in Table 7. The recovery of Th(IV) at 95% confidence level was 98.5±0.6%.

Table 6. Separation of Th(IV) from multi component mixtures

Multi component mixture	Recovery of Th(IV),* %
Co(II): 20 µg, Ni(II): 20 µg, Th(IV): 20 µg	99.2 ± 0.1
Ca(II): 100 µg, Y(III): 20 µg, Th(IV): 20 µg	99.1 ± 0.3
Mn(II): 20 µg, Co(II): 20 µg, Th(IV): 20 µg	99.0 ± 0.2
Cd(II): 20 µg, Mn(II): 50 µg, Th(IV): 20 µg	98.8 ± 0.3
Ca(II): 100 µg, K(I): 100 µg, La(III): 20 µg, Ce(IV): 12 µg, Th(IV): 20 µg	98.9 ± 0.3
Zn(II): 15 µg, Cu(II): 8 µg, Fe(III): 8 µg, Pb(II): 5 µg, Th(IV): 20 µg	99.1 ± 0.1
Ce(IV): 12 µg, La(III): 10 µg, Nd(III): 9 µg, Pr(III): 2.5 µg, Th(IV): 20 µg	98.8 ± 0.2

* Average of six replicate analysis with % R.S.D.

Table 7. Separation of Th(IV) from monazite sand

Th(IV) present in monazite sand, mg·g^{-1} (ICP-AES)	Th(IV) recovered,mg·g^{-1} (Spectrophotometry)*	Th(IV) recovered, % (Spectophotometry)*
91.68	90.30 ± 0.3	98.5 ± 0.3

Aqueous phase = monazite sample soln.
Organic phase = $2\cdot10^{-3}$M Cyanex302.
Stripping agent = 5M HCl.
* Average of triplicate analysis with % R.S.D.

Conclusions

The proposed method for extraction of Th(IV) using Cyanex302 in xylene is simple, easy, selective and reproducible for isolation and separation of Th(IV) from complex matrices with a relative standard deviation 0.4%.

References

1. V. I. Volk, A. Yu. Vakhrushin, S. L. Mamaev, J. Radioanal. Nucl. Chem., 46 (2000) 697.
2. E. Hesford, H. A. Mckay, D. Scargill, J. Inorg. Nucl. Chem., 4 (1957) 321.
3. J. C. Guyon, B. Madison, Mikrochim. Acta, 1 (1975) 117.
4. Y. M. Reza, E. M. Ebrahim, Iranian J. Chem. Chem. Eng., 22 (2003) 71.
5. B. Gupta, P. Malik, A. Deep, J. Radioanal. Nucl. Chem., 251 (2002) 451.
6. G. S. Desai, V. M. Shinde, J. Radioanal. Nucl. Chem., 154 (1991) 227.
7. N. G. Bhilare, V. M. Shinde, J. Radioanal. Nucl. Chem., 185 (1994) 243.
8. D. V. Koladkar, P. M. Dhadke, J. Radioanal. Nucl. Chem., 253 (2002) 297.
9. M. Curtui, I. Haiduc, J. Radioanal. Nucl. Chem., 136 (1994) 273.
10. M. Curtui, I. Haiduc, L. Haiduc, J. Radioanal. Nucl. Chem., 165 (1992) 95.
11. S. G. Sarkar, S. V. Bandekar, P. M. Dhadke, J. Radioanal. Nucl. Chem., 243 (2000) 803.
12. P. S. Mansingh, V. Chakrvortty, K. C. Dash, Radiochim. Acta, 73 (1996) 139.
13. W. A. Rickelton, R. J. Boyle, Solvent Extr. Ion Exch., 8 (1990) 783.
14. Wang Chun, Li Dequan, Solvent Extr. Ion Exch., 13 (1995) 503.
15. F. J. Welcher, The Analytical Uses of Ethylenediamine Tetraacetic Acid, D. Van Nostrand Co., Inc., New Jersey, 1978, p. 197.
16. F. D. Snell, Photometric and Fluorimetric Methods of Analysis, Part II, John Wiley and Sons, New York, 1978, p. 1820.
17. W. W. Scott, Standard Methods of Chemical Analysis, 5th ed., Vol. 1, D. Van Nostrand Co., Inc., New Jersey, p. 948.